



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ :

C01B 33/193

A1

(11) International Publication Number:

WO 00/46149

(43) International Publication Date:

10 August 2000 (10.08.00)

(21) International Application Number: PCT/EP00/00757

(22) International Filing Date: 1 February 2000 (01.02.00)

(30) Priority Data:

MI99A000197

3 February 1999 (03.02.99)

IT

(71) Applicant (for all designated States except US): ITAL-CEMENTI S.P.A. [IT/IT]; Via G. Camozzi, 124, I-24100 Bergamo (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): DE MARCO, Tiziana [IT/IT]; Via Lungo Brembo, 34, I-24035 Curno (IT). GRONCHI, Paolo [IT/IT]; Via Solari 2/a, I-20144 Milan (IT). CASSAR, Luigi [IT/IT]; Via Europa 42, I-20097 San Donato Milanese (IT).

(74) Agents: DE GREGORI, Antonella et al.; Ing. Barzanò & Zanardo Milano S.p.A., Via Borgonuovo, 10, I-20121 Milan (IT).

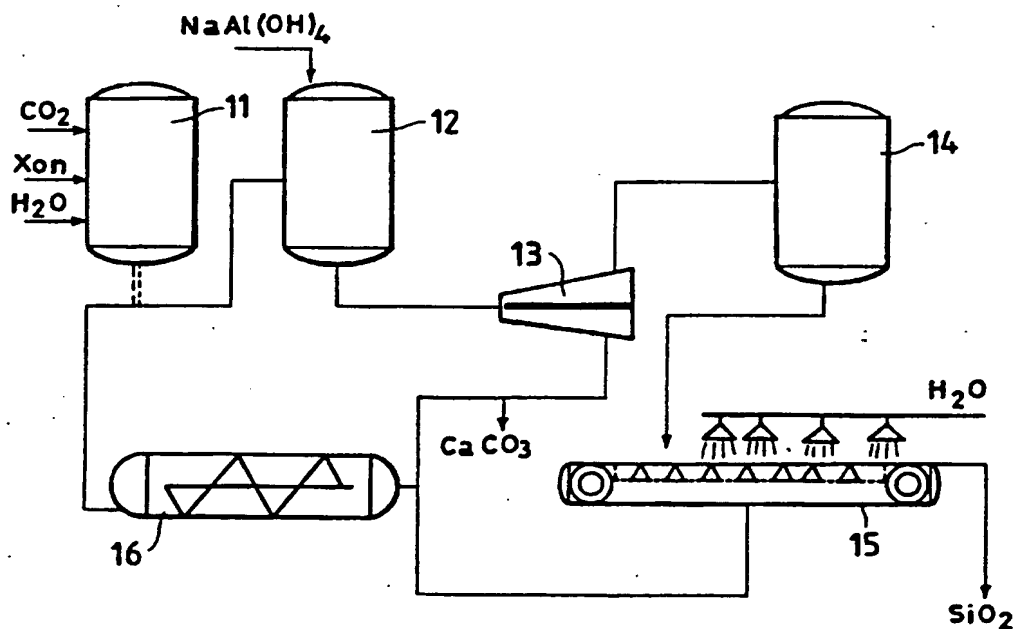
(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PROCEDURE FOR PREPARING SILICA FROM CALCIUM SILICATE



(57) Abstract

This invention concerns a procedure for preparing amorphous silica from calcium silicate and CO₂, with formation and separation of precipitate CaCO₃.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

"Procedure for preparing silica from calcium silicate."

This invention concerns a procedure for preparing amorphous silica from calcium silicate.

5 From the literature, many methods are known for obtaining amorphous silica from various materials. The starting materials used are generally silicates of alkaline metals, preferably sodium, as described for example in WO96/30301.

10 A particularly interesting starting material is calcium silicate.

Natural or artificial calcium silicates are low-cost materials which, by means of the reaction of CO_2 in water, allow solid mixtures of SiO_2 and CaCO_3 to be
15 obtained, products with a high added value.

However, the use of calcium silicates instead of silicates of alkaline metals, or particularly instead of sodium silicate, presents considerable problems due to the poor solubility of calcium silicate in water, in
20 comparison with sodium silicate.

An example of a procedure for obtaining silica and compounds of silica and calcium carbonate from calcium silicates is described in patent CA 1,122,779. That patent describes a procedure for obtaining silica, in

which the calcium silicate crystals are placed in contact with CO_2 in the presence of water and converted into silica, having the same configuration as crystals of silicate, and into particles of calcium carbonate
5 attached to the particles of amorphous silica. The SiO_2 - CaCO_3 mixture is not separable and so, to recover the silica, a treatment with mineral acids is carried out. The acid decomposes the calcium carbonate into CO_2 and calcium salts. The acid may be HCl , for example, thus
10 obtaining CO_2 and calcium chloride. It is then washed with water to eliminate the calcium salt, thus obtaining an aqueous suspension containing silica. However, with a procedure of this type the quantity of silica obtained is extremely low in comparison with the volumes of liquid
15 involved. There is therefore a low production rate per unit volume, which considerably penalises the process described even though it allows particularly pure silica to be obtained.

Moreover this procedure requires the use of an inorganic
20 acid and it is not possible to recover the CaCO_3 .

The aim of this invention is therefore to develop a procedure for obtaining amorphous silica from calcium silicate which presents high yield and a high production rate, along with high purity of the product.

A further aim of this invention is to obtain a process with a low degree of environmental pollution, since instead of mineral acids it uses CO_2 alone as the acid agent. A further aim of this invention is to recover
5 precipitate calcium carbonate in mild temperature and pressure conditions.

The aim of this invention is therefore a procedure for preparing amorphous silica comprising the following phases:

10 a) reaction of a calcium silicate with CO_2 in an aqueous environment with the formation of a suspension 1 of agglomerated particles of SiO_2 and CaCO_3 ;

b) treatment of the suspension 1 with a compound of aluminium, boron or zinc or mixtures of the same in a
15 neutral or basic environment, and formation of a solid phase 2 in a solution 3 containing particles of SiO_2 with nanometric dimensions;

c) separation of the solid phase 2 from the solution 3;
and

20 d) treatment of the solution 3 according to one of the following methods;

e) precipitation or drying;

f) gelation.

In the description and the claims of this invention the

expression "amorphous silica" means non crystalline silica which may be obtained in the form of a gel or in the form of a precipitate.

The reaction of phase a) of the process is carried out in an autoclave at a pressure between 0.3 MPa and 3 MPa and at a temperature between 10°C and 100°C. More particularly the phase a) is carried out at a pressure between 1.0 and 2.5 MPa and at a temperature between 15 and 40°C. Preferably the pressure is equal to 2 MPa and the temperature is equal to 20°C or 30°C.

The pH is a function of the CO₂ pressure and, around a pressure of 2 MPa, it stabilises around the value 5.2. The water/calcium silicate weight ratio may have any value, preferably between 16 and 6.4.

In these conditions of temperature, reagent concentration, pressure and pH, the reaction proceeds with the dissolution of the calcium silicate and concludes with the formation of an aqueous suspension of agglomerated particles of SiO₂ and CaCO₃.

The simultaneous precipitation of SiO₂ and CaCO₃ could be avoided by carrying out the reaction with low loads of calcium silicate (water/calcium silicate weight ratio greater than 16), obtaining a precipitate composed prevalently of CaCO₃ in the presence of a solution

containing nanometric particles of silica. In this system, however, the quantity of silica in the solution would be too low and therefore not sufficient for an industrial realisation of the process.

5 Even if the load of silica were increased, the concentration of silica in the solution would not exceed 10 kg/m³ (± 4); moreover in these experimental conditions this solution is a metastable phase which tends to gel quickly, preventing the separation of the silica from the
10 precipitated solid composed of CaCO₃.

It is known from the literature that the stabilising of a solution containing amorphous silica in particles is a function of the increase of the pH up to alkaline values ≥ 9.5 or of the reduction of the concentrations of
15 alkaline ions (R.K. Iler, The Chemistry of Silica, 1979). Alkaline pH values may be easily obtained by adding, for example, NaOH, while the problem of reaching higher concentrations of silica in the aqueous phase is more difficult to solve.

20 In order to solve this problem, the procedure according to this invention is characterised by the phase b), that is the reaction of the aqueous suspension 1, coming from the acid dissolution, with a compound of aluminium, boron or zinc or mixtures of the same in a neutral or basic

environment.

The neutral or basic environment ($\text{pH} \geq 7$) is preferably realised using a solution of hydroxides or salts of alkaline metals or alkaline earth metals. In particular, 5 the solution is an aqueous solution of hydroxides of alkaline metals or alkaline earth metals and, even more particularly, the solution is an aqueous solution of sodium hydroxide.

The compound of aluminium, boron or zinc is preferably a 10 salt chosen among aluminates, borates or zincates. In particular, the salt is an alkaline aluminate or an alkaline earth aluminate and, even more preferably, the salt is a sodium aluminate.

The treatment in phase b) is decisive for the development 15 of the entire process, being essential for the separation of silica from carbonate.

This reaction allows the modification of the silica surface and the increase of its concentration in the solution 3 at least up to 50-60 kg/m³.

20 The solution 3 which forms in phase b) contains particles of silica of with nanometric dimensions defined as "primary particles". In particular the dimensions of the primary particles are between 1 and 100 nanometers.

The third phase c) of the process includes the separation

of the solid phase 2 rich in calcium carbonate from the solution 3 containing silica.

The separation phase c) is carried out by means of any of the known methods for phase separations, preferably it is
5 done by centrifugation; if the separated solid mixture still contains silica aggregated with carbonate, it may be recycled and again subjected to the treatment with aluminate.

The fourth phase d) of the process contemplates treatment
10 of the solution 3 containing silica, according to one of the following methods:

according to the first method, indicated as e), the treatment may be carried out preferably by drying or precipitation, obtaining precipitated silica.

15 Precipitation may come about by means of variation of the chemical-physical parameters, with or without the addition of precipitating agents.

In particular, precipitation may come about with the addition of CO_2 , at environment pressure and temperature.

20 Afterwards there is the separation of the phases that formed during the precipitation phase. In particular, this separation may be achieved by means of filtration. The solid kept back by the filter is washed until a neutral pH (about 7) is reached in the washing waters.

According to the method f), the treatment leads to gelation, followed by evaporation of the liquid phase. The gelation treatment, as known in the art, is achieved by acidification, for example by adding CO₂, at
5 environment temperature, to a pH lower than 7. Depending on the temperature at which evaporation takes place, cryogel, aerogel or xerogel may be obtained.

It is to be noted that the first phase of the process (reaction of calcium silicate with CO₂) and the second
10 phase of the process (treatment with salts containing aluminium, boron or zinc) may also be simultaneous and carried out in the same reactor, adequately checking the pH with suitable buffers.

A further aim of this invention is the use of the
15 amorphous silica obtained with the procedure according to this invention as an additive in mixtures for tyres with low rolling resistance force or as a mineral addition in High Performance Concretes (HPC), such as high or very high strength concrete (preferably more than 100 MPa).

20 The term High Performance Concretes (HPC) identifies a class of cement mixes with characteristics of high mechanical strength (compression strength R_c at 28 days greater than 60 MPa).

An example of HPC is a high-strength concrete known as

DSP (densified with small particles). In this material the microstructure of the cement matrix is densified by adding silica fume. In DSP it is possible to reach Rc at 28 days greater than 100 MPa.

5 In particular, also the compound material composed of the mixture of silica and calcium carbonates, obtained according to the procedure of this invention, may be used directly as an additive in mixtures for tyres or in high-performance concretes, for example in a high-strength
10 concrete (DSP).

Moreover the amorphous silica obtained with the procedure according to this invention may be used in many other sectors; it may be used as a reinforcing load in rubber and other organic polymers, as a pigment partially
15 substituting TiO_2 in the production of paper and coating, as a dimmer in the water paint and varnishes industry, as a thinner in solid formulations, as an anti-blocking agent to prevent adhesion between smooth surfaces, as an anti-binding agent or a catalytic support.

20 The principal advantage of the procedure according to this invention is that of obtaining high-purity amorphous silica by means of a process with a low environmental impact, presenting high production rate and high yield at the same time.

A further advantage of this invention is that of obtaining precipitated calcium carbonate in the form of fine particles.

The starting material may be natural, synthetic,
5 crystalline and amorphous calcium silicates.

The starting material may also be clinker of Portland cement. By clinker of Portland cement is meant a hydraulic material which must be composed of at least two thirds in mass of calcium silicates ($3\text{CaO} \cdot \text{SiO}_2$) and
10 ($2\text{CaO} \cdot \text{SiO}_2$). The remaining part contains aluminium oxide (Al_2O_3), ferric oxide (Fe_2O_3) and other oxides. The CaO/SiO_2 mass ratio must not be less than 2.0. The magnesium oxide (MgO) content must not exceed 5.0% of the mass.

15 Clinker of Portland cement is obtained by the baking, at least as far as sintering, of a precisely established mixture of raw materials (raw meal, paste or suspension) containing CaO , SiO_2 , Al_2O_3 and small quantities of other materials. The raw meal, paste or suspension must be
20 finely ground, closely mixed and therefore be homogeneous. The clinker of Portland cement used as the starting material for the process of this invention is preferably rich in silicates and contains low percentages of the other oxides.

A calcium silicate which can be used as the starting material in the process according to this invention is xonotlite ($\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$) which may be synthesised in hydrothermal conditions according to the following
5 reaction: $\text{CaO}/\text{Ca}(\text{OH})_2 + \text{silica (or sand or quartz)} + \text{H}_2\text{O}$
+ minor components (silica fume, bentonite) are made to react in the presence of water vapour at a temperature between 176 and 240°C, at a pressure of 1.4 - 1.5 MPa, for a time of 1 to 24 hours, preferably from 1 to 7
10 hours, with a molar ratio CaO/SiO_2 between 0.65 and 1 and with a specific surface of the reagents from 18 to 22 m^2 . After cooling, filtration and washing, crystals of xonotlite are obtained.

It is also possible to use as starting material a calcium
15 silicate which may be crystalline or prevalently amorphous. In particular, feeding pure quartz with a diameter < 40 μm , CaO (containing about 7% CaCO_3 , with diameter < 25 μm), silica fume and bentonite in a one-litre stainless steel autoclave, lined, with agitator,
20 and letting it react at a temperature between 195 and 200°C for 24 hours at a pressure of 1.53 MPa, prevalently crystalline calcium silicate is obtained. Instead, using reaction times of 4-7 hours, prevalently amorphous silicates are obtained with a surface area equal to

approximately 100 m²/g.

Another calcium silicate that may be used as a starting material is tobermorite.

The following tables 1 and 2 list some conditions of synthesis of xonotlite (xon-1, xon-2, xon-3) and of amorphous hydrate calcium silicates (CSH-1, CSH-2, CSH-3, CSH-4 and CSH-5) which may be used as starting materials for the procedure according to this invention.

Table 1.

Feed	XON-1	XON-2	XON-3
CaO	55.9%	51.35%	51.3%
SiO ₂	43.9%	48.5%	48.5%
Silica fume	0.2%	0.1%	0.2%
Bentonite	0.05%	0.05%	0.05%
H ₂ O	480%	1200%	1200%
Ca/Si	1.12	0.98	1.00
H ₂ O/dry	4.8	12.00	12.00
Temperature	185°C	195°C	200°C
Pressure	1.1 MPa	1.4 MPa	1.5 MPa
Reaction time	24 h	7 h	4 h
Pressurisation	2.5 h	2.5 h	2.5 h
Depressurisation	6 h	6 h	6 h

ion			
-----	--	--	--

Table 2

Feed	CSH-1	CSH-2	CSH-3	CSH-4	CSH-5
CaO	52.9%	52.9%	48.9%	51.3%	51.3%
SiO ₂	46.8%	46.8%	50.9%	48.5%	48.5%
Silica fume	0.2%	0.2%	0.1%	0.2%	0.2%
Bentonite	0.05%	0.05%	0.05%	0.05%	0.05%
H ₂ O	480%	480%	500%	480%	970%
Ca/Si	1.07	1.07	0.89	1.00	1.00
H ₂ O/dry	4.8	4.8	5.0	4.8	9.7
Temperature	175°C	130°C	197°C	198°C	198°C
Pressure	0.85 MPa	0.3 MPa	1.4 MPa	1.4 MPa	1.4 MPa
Reaction time	7 h	0 h	4 h	2 h	4 h
Pressurisation	2.5 h	1.5 h	2.5 h	2.5 h	2.5 h
Depressurisation	6 h	6 h	6 h	6 h	6 h

5 Figure 1 shows an exemplificative diagram representing a particular embodiment of a system for carrying out the procedure according to this invention.

In the diagram shown in figure 1, 11 indicates the

dissolving reactor, 12 the alumination reactor, 13 the solid-liquid centrifuge, 14 the drier or the precipitation reactor, 15 the washing-drying unit and 16 the mixing unit.

5 According to this diagram, CO₂, xonotlite or calcium silicate and H₂O are loaded at 11 and the dissolution reaction then occurs by acid attack of the silicate; the product obtained arrives at 12 where it is treated with preconstituted solutions of sodium aluminate. At 13
10 there is then the separation by centrifugation of a solid phase and a liquid phase.

The solid phase, coming from 13, which by spectroscopic analysis reveals the presence of carbonates, may be sent by means of the mixer 16 to the alumination reactor 12
15 where it is again treated with sodium aluminate, while the liquid phase is sent to the reactor 14. The dried/precipitated product arrives at the washing-drying unit 15, from which the final product, silica, is obtained.

20 The solid phase, coming from 13, may also be sent back to the dissolution reactor 11.

The characteristics and the advantages of the procedure according to this invention will be better understood from the following detailed and exemplificative

description.

Example 1A

25 g of (pure) Xonotlite coming from hydrothermal synthesis and having a specific surface BET equal to 54 m²/g were suspended in 400 ml of water (volume H₂O/g of xonotlite = 16) and the suspension was kept in agitation in a one-litre stainless steel autoclave. The reactor was pressurised with CO₂ at 2.0 MPa and the temperature kept at 20°C. The dissolution reaction was made to proceed for 1 hour, up to a pH of about 5.2. The autoclave was then depressurised and the suspension obtained was filtered. The solid obtained from filtration was composed of the mixture of silica and precipitated calcium carbonate, with percentages (of the dry product) of respectively 51.4% and 48.6%.

This mixture was treated with an aqueous solution of sodium aluminate, prepared from NaOH in quantity 1 M and Al in quantity 0.01 M, at environment temperature, under agitation, for 2 hours.

After centrifugation and drying of the supernatant liquid (at pH = 10), a dry residue was obtained (110°C, 4 hours) which on IR analysis revealed an intense and broad absorption at 1015 cm⁻¹, which may be attributed to silicoaluminate entities. The thermal analysis agrees

with the respective spectrophotometric analysis and revealed a high weight loss (about 2.5%) which may be attributed to the loss of free and bonded water ($T \leq 400^{\circ}\text{C}$). The weight loss at $T > 400^{\circ}\text{C}$ is very low (5-
5 10%) and indicates the presence of a low percentage of carbonate and the transformation of the hydroxides present into oxides.

The trend of the curves is very different, for example, from the one that may be obtained analysing the dry
10 residue of the colloidal phase obtained directly after the acid dissolving attack of the phase a).

After treatment of the $\text{CaCO}_3/\text{SiO}_2$ mixture with a solution of sodium aluminate, the solid obtained from drying of the supernatant liquid presented on spectroscopic analysis
15 some absorption bands characteristic of carbonates.

Once washed in water, the IR analysis allowed it to be revealed that these absorption bands were found in the washing waters and no longer in the solid residue, which was therefore silica with high purity.

20 The precipitated silica obtained after treatment with sodium aluminate is impure with Na_2CO_3 , which is water-soluble and can therefore be removed with washing.

The characterisation of the precipitated silica obtained is shown in the following table 3.

Table 3: Characterisation of precipitated silica (Example 1A).

	• Specific surface BET (m^2/g) 63;
5	• pH (5% aqueous solution) 7;
	• loss at 105°C (%) 4.5%;
	• loss to fire - 1000°C 11.7%;
	• Analysis of the calcinated product at 1000°C for 2 hours:
10	- SiO_2 (%) 96.5;
	- Al_2O_3 (%) 0.65;
	- Na_2O (%) 1.35;
	- CaO (%) 1.4;
	- Fe_2O_3 (%) 0.01

15

The specific surface B.E.T. is determined according to the BRUNAUER-EMMET-TELLER method described in the Journal of the American Chemical Society, vol. 60, page 309, February 1938 and according to standard ISO 9277-95.

20 The pH is determined according to standard ISO 787/9 (pH of a 5% suspension in H_2O).

Example 1B

The solid residue coming from centrifugation in the

previous example 1A was again suspended in water and treated with sodium aluminate and afterwards centrifuged and dried. This further treatment with sodium aluminate allowed a further recover of silica, allowing a possible
5 exhaustion of the silica present in the starting mixture. The characterisation of the precipitated calcium carbonate, obtained after three treatments with sodium aluminate, is shown in the following table 4.

Table 4: Characterisation of precipitated CaCO_3 (Example
10 1B).

- | |
|---|
| <ul style="list-style-type: none">• Specific surface BET (m^2/g) 9;• pH (5% aqueous solution) 10;• loss at 105°C (%) ≤ 2; |
|---|

15 Example 2

A mixture composed of Xonotlite and Tobermorite in weight ratios 70:30 was suspended in water (70 g of mixture in 450 g of water) and the suspension kept in agitation in a one-litre stainless steel autoclave. The reactor was
20 pressurised with CO_2 at 2.0 MPa and the temperature kept at 30°C . The reaction was carried out for 30 minutes, always in agitation, up to a pH of about 5.2. The autoclave was then depressurised and an aqueous solution of sodium aluminate, prepared from NaOH in quantity 3 M

and Al in granules in quantity 0.03 M, was directly added in the reactor. The suspension was kept at environment pressure and temperature, under agitation, for 2 hours. After that period, the suspension in the reactor is
5 centrifuged. Into the liquid, which has a pH value of 11, separated from the solid phase and kept under agitation, CO₂ is bubbled until a pH of 7.5 is reached. The solid and liquid are then separated by filtration. The solid kept back by the filter is washed with
10 deionised water (until a pH of 7 is obtained in the washing water). The solid obtained is composed of precipitated silica with high purity and it has the characteristics listed in table 5.

Example 3

15 A mixture composed of Xonotlite and Tobermorite is treated substantially following the description in example 2 up to the stage in which the suspension in the reactor is centrifuged. Into the liquid, separated from the solid phase and kept under agitation, CO₂ is bubbled
20 until a pH of 6.5 is reached. The solution gels and is separated by filtration. The gel solid kept back by the filter is washed with deionised water (until a pH of 7 is obtained in the washing water), then dried and crushed. The specific surface BET of the amorphous silica thus

obtained is 90 m²/g:

Table 5: Characterisation of precipitated silica (Example 2).

	• Specific surface BET (m ² /g)	160;
5	• pH (5% aqueous solution)	7;
	• loss at 105°C (%)	4.3;
	• loss to fire - 1000°C (%)	12;
	• Analysis of the calcinated product at 1000°C for 2 hours:	
10	- SiO ₂ (%)	97;
	- Al ₂ O ₃ (%)	0.7;
	- Na ₂ O (%)	1.05;
	- CaO (%)	1.24;
	- Fe ₂ O ₃ (%)	0.01
15		

The following examples refer to a number of tests of application.

Example 4

Using the precipitated silica obtained in example 1A, DSP
20 concrete having the following composition was prepared:

- Cement CEM I 52.5 (Ultracem R) 642 g;
- Aggregate: spherical quartz (max. diam. = 1200 g;
3.2 mm)

- Precipitated silica (S.S. BET = $63 \text{ m}^2/\text{g}$) 80 g;
- Super-fluidifying acrylic additive 44 g;
(Superflux 2000 AC)
 - Mixing water 149 g;
 - Water/binder* ratio 0.25;
 - Aggregate/binder ratio 1.66

* binder = cement + precipitated silica

With this mixture three test pieces with dimensions $40 \times 40 \times 160 \text{ mm}$ were prepared and were subjected to accelerated curing (24 hours in water at 80°C).

- 5 The mechanical strength values measured on the test pieces were:

$R_c = 119 \text{ MPa};$

$R_f = 18.7 \text{ MPa}.$

Example 5

- 10 A mixture for tyres was prepared containing precipitated silica from example 2.

The specific surface BET of the silica was $160 \text{ m}^2/\text{g}$.

The mixture was prepared with 40 parts of silica to every 100 parts of styrene butadiene rubber (SBR) and presents

- 15 the following characteristics:

Ultimate elongation =	720%;
Ultimate tensile stress =	16 MPa;
Modulus at 500% =	6.5 MPa.

So, as previously indicated and shown, the precipitated silica obtained with the procedure according to this invention may be successfully used in high-performance concretes, such as high or very high strength concretes (DSP) or it may be added to mixtures for tyres with low rolling resistance force.

It was also found that both the solid phase 2 and the solution 3 obtained at the end of phase c) of the procedure according to this invention may be used with excellent results as additives in mixtures for tyres and in high performance concretes (for example high or very high strength concretes).

CLAIMS

1. Procedure for preparing amorphous silica comprising the following phases:
 - a) reaction of a calcium silicate with CO_2 in an aqueous environment with the formation of a suspension 1 of agglomerated particles of SiO_2 and CaCO_3 ;
 - b) treatment of the suspension 1 with a compound of aluminium, boron or zinc or mixtures of the same in a neutral or basic environment, and formation of a solid phase 2 in a solution 3 containing particles of SiO_2 with nanometric dimensions;
 - c) separation of the solid phase 2 from the solution 3;
 - d) treatment of the solution 3 according to one of the following methods;
 - e) precipitation or drying;
 - f) gelation.
2. Procedure according to claim 1, wherein the reaction of phase a) is carried out in an autoclave at a pressure between 0.3 MPa and 3 MPa and at a temperature between 10°C and 100°C .
3. Procedure according to claim 2, wherein the pressure is between 1.0 and 2.5 MPa and the temperature is between 15 and 40°C .
4. Procedure according to claim 3, wherein the pressure

is equal to 2 MPa and the temperature is equal to 20°C or 30°C.

5. Procedure according to claim 1, wherein the compound of aluminium, boron or zinc is a salt chosen among
5 aluminates, borates or zincates.

6. Procedure according to claim 5, wherein the salt is an alkaline aluminate or an alkaline earth aluminate

7. Procedure according to claim 5, wherein the salt is a sodium aluminate

10 8. Procedure according to claim 1, wherein the neutral or basic environment is realised using a solution of hydroxides or salts of alkaline metals or alkaline earth metals.

9. Procedure according to claim 8, wherein the solution
15 is an aqueous solution of hydroxides of alkaline metals or alkaline earth metals.

10. Procedure according to claim 8, wherein the solution is an aqueous solution of sodium hydroxide.

11. Procedure according to claim 1, wherein the particles
20 of silica in the solution 3 have dimensions between 1 and 100 nanometers.

12. Procedure according to claim 1, wherein the separation phase c) is carried out by centrifugation.

13. Procedure according to claim 1, wherein the solid

phase 2 coming from the separation phase c) is recycled so as to be again subjected to treatment with sodium aluminate as in phase b).

14. Procedure according to claim 1, wherein the
5 precipitation treatment e) is carried out with the addition of CO₂, at environment pressure and temperature.

15. Procedure according to claim 14, wherein the phases that formed during the precipitation phase are separated by filtration and the solid kept back by the filter is
10 washed until a neutral pH is reached in the washing waters

16. Procedure according to claim 1, wherein the gelation
treatment f) is achieved by acidification, for example by
adding CO₂, at environment temperature, to a pH lower
15 than 7, and is followed by the evaporation of the liquid phase.

17. Precipitated silica that can be obtained with the procedure according to one of the claims from 1 to 16, characterised by having purity $\geq 96\%$

20 18. Use of the silica obtained with the procedure according to any one of the claims from 1 to 16 as an additive in mixtures for tyres.

19. Use of the silica obtained with the procedure according to any one of the claims from 1 to 16 as an

additive in High Performance Concretes.

20. Use according to claim 19 in high or very high strength concretes (DSP).

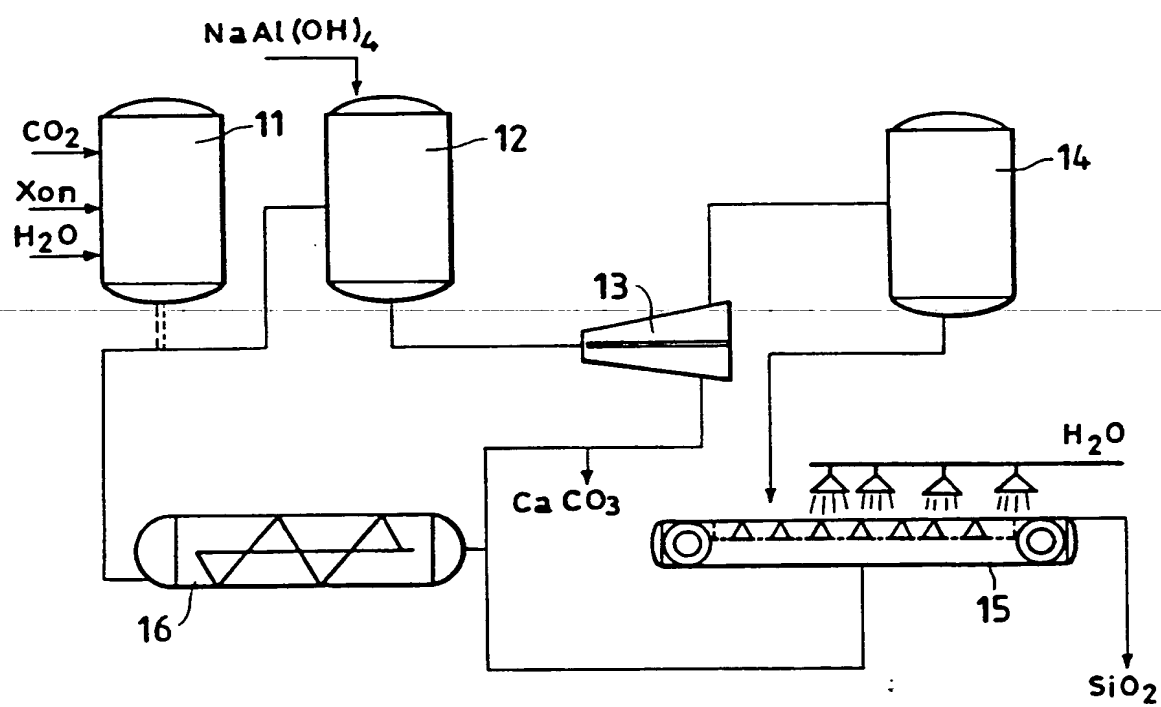
21. Use of the silica obtained with the procedure
5 according to any one of the claims from 1 to 16 as a reinforcing load in rubber and other organic polymers, as a pigment partially substituting TiO_2 in the production of paper and coating, as a dimmer in the water paint and varnishes industry, as a thinner in solid formulations,
10 as an anti-blocking agent to prevent adhesion between smooth surfaces, as an anti-binding agent or a catalytic support.

22. Use of the solid phase 2, composed of silica and calcium carbonate, obtained after phase c) of the
15 procedure according to claim 1, as an additive in mixtures for tyres.

23. Use of the solid phase 2, composed of silica and calcium carbonate, obtained after phase c) of the procedure according to claim 1, as an additive in High
20 Performance Concretes.

24. Use according to claim 23 in high or very high strength concretes (DSP).

25. Composition of precipitated silica which may be obtained according to the procedure of claim 1.

Fig.1

JC17 Rec'd PCT/PTO 3 1 JUL 2001

INTERNATIONAL SEARCH REPORT

Application No
PCT/EP 00/00757A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B33/193

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 330 519 A (TAKAHASHI AKIRA ET AL) 18 May 1982 (1982-05-18) column 10, line 4 -column 12, line 60 & CA 1 122 779 A cited in the application	1
A	PATENT ABSTRACTS OF JAPAN vol. 016, no. 548 (C-1005), 18 November 1992 (1992-11-18) & JP 04 209717 A (NIHON INSHIYUREESHIYON KK), 31 July 1992 (1992-07-31) abstract	1

-/-

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

16 May 2000

Date of mailing of the international search report

05/06/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Clement, J-P

INTERNATIONAL SEARCH REPORT

national Application No
PCT/EP 00/00757

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 197748 Derwent Publications Ltd., London, GB; Class L02, AN 1977-85887Y XP002137760 & JP 52 126695 A (OSAKA PACKING SEIZOSHO KK), 24 October 1977 (1977-10-24) abstract</p>	1
A	<p>DATABASE WPI Section Ch, Week 197652 Derwent Publications Ltd., London, GB; Class E33, AN 1976-96970X XP002137761 & JP 51 129424 A (OSAKA PACK MFG KK), 11 November 1976 (1976-11-11) abstract</p>	1

INTERNATIO SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/00757

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4330519	A	18-05-1982	JP 1106213 C	30-07-1982
			JP 51125699 A	02-11-1976
			JP 55014809 B	18-04-1980
			JP 1126024 C	14-12-1982
			JP 52008023 A	21-01-1977
			JP 55023788 B	25-06-1980
			JP 1128121 C	24-12-1982
			JP 52008024 A	21-01-1977
			JP 55023789 B	25-06-1980
			AU 502847 B	09-08-1979
			AU 1229376 A	13-10-1977
			CA 1097030 A	10-03-1981
			CA 1122778 A	04-05-1982
			CA 1122779 A	04-05-1982
			CA 1123172 A	11-05-1982
			CA 1122780 A	04-05-1982
			DE 2612281 A	20-01-1977
			FR 2313315 A	31-12-1976
			FR 2332955 A	24-06-1977
			GB 1511125 A	17-05-1978
			IT 1058526 B	10-05-1982
			NL 7603156 A,B,	28-09-1976
			SE 420596 B	19-10-1981
			SE 7603441 A	26-09-1976
			SE 7908472 A	12-10-1979
			US 4230765 A	28-10-1980
JP 04209717	A	31-07-1992	JP 1982394 C	25-10-1995
			JP 6102533 B	14-12-1994
JP 52126695	A	24-10-1977	JP 1397069 C	24-08-1987
			JP 61058436 B	11-12-1986
JP 51129424	A	11-11-1976	JP 1184225 C	27-12-1983
			JP 55023790 B	25-06-1980

PATENT COOPERATION TREATY

PCT

REC'D 27 APR 2001

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 81668	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP00/00757	International filing date (day/month/year) 01/02/2000	Priority date (day/month/year) 03/02/1999
International Patent Classification (IPC) or national classification and IPC C01B33/193		
Applicant ITALCEMENTI S.P.A. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 8 sheets, including this cover sheet.

- ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 29/08/2000	Date of completion of this report 25.04.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Krafka, B Telephone No. +49 89 2399 8140 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/00757

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-22 as originally filed

Claims, No.:

1-25 as originally filed

Drawings, sheets:

1/1 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/00757

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-16,18-20,22-24
	No:	Claims	17,21,25
Inventive step (IS)	Yes:	Claims	1-16,18,22
	No:	Claims	19-20, 23-24
Industrial applicability (IA)	Yes:	Claims	1-25
	No:	Claims	

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1) Reference is made to the following documents:

D1: US-A-4 330 519 (TAKAHASHI AKIRA ET AL) 18 May 1982 (1982-05-18) & CA 1 122 779 A cited in the application

2) Novelty - Art. 33 (1) and (2) PCT

2.1. Claim 17 claims precipitated silica as a product, having purity $\geq 96\%$.

Numerous variants of manufacturing processes for precipitated silica of high purity are commonly known in the art. For example, it is remarked, that in the description, page 1 line 21 - page 2 line 18 the process of CA 1 122 779 is cited, stating on page 2 lines 17-18, that the process described allows particularly pure silica to be obtained. Additionally, D1 discloses a process to produce amorphous silica of high purity (column 2 lines 56-57), demonstrated in numerous examples, e.g. in example 2 purity is 99.3%. D1 also discloses composite materials, in which the silica is incorporated (column 2 lines 28-37). Furthermore, D1 discloses the use of said silica for various purposes, e.g. as catalyst carrier (column 5 lines 25-47). Therefore, it cannot be seen in which way Claims 17, 21 and 25 could establish novel subject-matter.

2.2. The manufacturing process as claimed in Claim 1 is considered to be novel and inventive over the processes of prior art (see, however, Item VIII). In the description, the applicant defines a process in which, among other process steps, an aqueous suspension of agglomerated particles of SiO_2 and CaCO_3 is treated with salts chosen among aluminates, borates or zincates, which results in a modification of the silica surface and an increase of its solubility in the solution. The solid phase rich in calcium carbonate can then be easily separated from the solution containing silica. Such a process step is not known from the prior art. However, reaction parameters which seem to be crucial for the success of said process are not defined in Claim 1 but are only given as optional features in subsequent dependant claims. The applicant's attention is therefore drawn to the argumentation concerning clarity of Claim 1 under Item VIII.

- 2.3. Claims 2-16 are dependent on claim 1 and as such also meet the requirements of the PCT with respect to novelty.
- 2.4. Even if the claimed process is novel and inventive, this is still not sufficient to establish novelty for the product per se and its intended use, as long as the product does not exhibit features which clearly distinguish it from the prior art and as long as the intended use is known for SiO_2 .
- 2.5. The use of precipitated silica having purity $\geq 96\%$ or of a solid phase comprising silica and calcium carbonate as additives in mixtures for tyres, in High Performance Concretes or high strength concretes has not been disclosed in the prior art. Therefore, claims 18-20 and 22-24 are considered to define novel subject-matter.

3) Inventive Step - Art. 33 (1) and (3) PCT

- 3.1. The technical problem underlying the present invention can be seen in providing an alternative procedure for preparing amorphous silica from calcium silicate. The recovery of the silica by treatment with mineral acids should be avoided, as this leads to extremely low quantities of silica obtained in comparison with the volumes of liquid involved, and the recovery of CaCO_3 , the side product, is not possible. This problem is overcome by the present invention by treating the aqueous suspension of agglomerated particles of SiO_2 and CaCO_3 , which results from the reaction of calcium silicate with CO_2 in an aqueous environment, with a salt chosen among aluminates, borates, zincates, or mixtures of the same. This reaction allows the modification of the silica surface and the increase of its concentration in the solution. The solid phase rich in calcium carbonate is separated from the solution containing silica.
- Documents D1 is considered to represent the closest prior art.
- 3.2. From none of the prior art document it appears to be obvious to treat the aqueous suspension of agglomerated particles of SiO_2 and CaCO_3 with a salt chosen among aluminates, borates, zincates, or mixtures of the same, in order to modify the silica surface and to thereby increase its concentration in the solution. Therefore, the process as claimed in independent claim 1 and in claims 2-16,

dependent on claim 1, is regarded as establishing inventive subject-matter.

- 3.3. The use of precipitated silica having purity $\geq 96\%$ or of a solid phase comprising silica and calcium carbonate as additives in mixtures for tyres has not been suggested in the prior art. Furthermore, none of the prior art documents cited above contains a hint that such kind of materials could be used in the fabrication of tyres at all. This application does not appear to lie within the scope of possible uses a person skilled in the art would take into consideration. Therefore, an inventive step is acknowledged for the subject-matter of claims 18 and 22.
- 3.4. The product of D1, which has been demonstrated to be the same as the product of the present application (see 2.1.), can be used as an additive for cements (column 5 line 29). It cannot be seen in which way the use of said silica in High Performance concretes or in high or very high strength concretes (DSP), as claimed in Claims 19 and 20, could lead to a surprising technical effect of the silica, which would be distinctively different from the technical effect achieved by the silica in D1. Therefore, an inventive step cannot be recognised for the subject-matter of Claims 19 and 20.
- 3.5. Concretes generally contain CaCO_3 and silicates. It is not clear, what technical effect could be achieved by adding a product containing just the same two constituents to concrete. Said feature is thus merely one of several straightforward possibilities from which the skilled person would select, in accordance with circumstances, without the exercise of inventive skill. Therefore, an inventive step is also not apparent for the subject-matter of Claims 23 and 24.

Re Item VII

Certain defects in the international application

- a. The terms "CEM I 52.5 (Ultracem R)" (page 20 line 21) and "Superflux 2000 AC" (page 21 line 3) employed in the description and appearing to be registered trade marks have no precise meaning as they are not internationally accepted as standard descriptive terms, thereby rendering the definition of the subject-matter of the description unclear (Article 6 PCT).

R Item VIII

Certain observations on the international application

- a. Claim 1 is unclear as to the subject-matter it refers to.
- "a compound of aluminium, boron or zinc": the description (page 6 lines 9-19) conveys the impression, that as said compound a salt should be chosen among aluminates, borates or zincates, in order to modify the silica surface and increase its concentration in the solution. Particles of insoluble Al_2O_3 for example, also falling within the scope of Claim 1 as presently drafted, do not seem to provide the technical effect mandatory for the invention claimed.
 - "a calcium silicate": this vague and imprecise term casts doubt as to whether this feature is sufficiently limited in scope to enable a person skilled in the art to carry out the invention. D1, column 2 line 65 - column 3 line 57 teaches the influence of the crystalline appearance of the silicate crystals on size and shape of the silica particles produced.
 - "an aqueous environment": this wording is too broad, as it does not unambiguously define that it is the suspension itself which is aqueous. Same applies to the term "neutral or basic environment".
 - "treatment": any sort of measure like freezing or stirring, which do not appear to be suitable to obtain the intended product, fall within the scope of this term.
 - "nanometric dimensions": concrete reaction conditions (temperature, reagent concentration, pressure and pH) appear to be missing also in step b) of Claim 1 to ensure formation of nanometer sized SiO_2 to ensure the required solubility.
 - "precipitation", "drying", "gelation": in order to ensure the amorphous nature of the product it appears to be indispensable to delimit the reaction parameters under which said process features are carried out.
 - Finally, the wording "procedure (..) comprising the following phases" does not make clear whether the process steps a) - f) have to be carried out in a certain order.

Summarising, it is outlined that a concrete significance in terms of a clearly defined matter for which protection is sought is not provided because the technical features necessary to perform the claimed invention (some of which are, at present, given in dependent claims) are not as a whole included in independent process claim 1.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP00/00757

- b. The wording of Claim 16 is unclear as it is not clear if only "adding of CO₂" is an optional feature, or if "for example" also refers to the following features of temperature and pH.
- c. In the term "max. diam. = 1200 g; 3.2 mm" it is unclear what the expression of weight is standing for.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 81668	FOR FURTHER ACTION		see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
International application No. PCT/EP 00/00757	International filing date (day/month/year) 01/02/2000	(Earliest) Priority Date (day/month/year) 03/02/1999	
Applicant ITALCEMENTI S.P.A.			

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☒ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

1
☐ None of the figures.



INTERNATIONAL SEARCH REPORT

National Application No

PCT/EP 00/00757

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B33/193

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 330 519 A (TAKAHASHI AKIRA ET AL) 18 May 1982 (1982-05-18) column 10, line 4 -column 12, line 60 & CA 1 122 779 A cited in the application	1
A	PATENT ABSTRACTS OF JAPAN vol. 016, no. 548 (C-1005), 18 November 1992 (1992-11-18) & JP 04 209717 A (NIHON INSHIYUREESHIYON KK), 31 July 1992 (1992-07-31) abstract	1

	-/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

16 May 2000

Date of mailing of the international search report

05/06/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Clement, J-P

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/00757

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p> DATABASE WPI Section Ch, Week 197748 Derwent Publications Ltd., London, GB; Class L02, AN 1977-85887Y XP002137760 & JP 52 126695 A (OSAKA PACKING SEIZOSHO KK), 24 October 1977 (1977-10-24) abstract </p>	1
A	<p> DATABASE WPI Section Ch, Week 197652 Derwent Publications Ltd., London, GB; Class E33, AN 1976-96970X XP002137761 & JP 51 129424 A (OSAKA PACK MFG KK), 11 November 1976 (1976-11-11) abstract </p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/00757

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4330519	A	18-05-1982	JP 1106213 C	30-07-1982
			JP 51125699 A	02-11-1976
			JP 55014809 B	18-04-1980
			JP 1126024 C	14-12-1982
			JP 52008023 A	21-01-1977
			JP 55023788 B	25-06-1980
			JP 1128121 C	24-12-1982
			JP 52008024 A	21-01-1977
			JP 55023789 B	25-06-1980
			AU 502847 B	09-08-1979
			AU 1229376 A	13-10-1977
			CA 1097030 A	10-03-1981
			CA 1122778 A	04-05-1982
			CA 1122779 A	04-05-1982
			CA 1123172 A	11-05-1982
			CA 1122780 A	04-05-1982
			DE 2612281 A	20-01-1977
			FR 2313315 A	31-12-1976
			FR 2332955 A	24-06-1977
			GB 1511125 A	17-05-1978
			IT 1058526 B	10-05-1982
			NL 7603156 A, B,	28-09-1976
			SE 420596 B	19-10-1981
			SE 7603441 A	26-09-1976
			SE 7908472 A	12-10-1979
			US 4230765 A	28-10-1980
JP 04209717	A	31-07-1992	JP 1982394 C	25-10-1995
			JP 6102533 B	14-12-1994
JP 52126695	A	24-10-1977	JP 1397069 C	24-08-1987
			JP 61058436 B	11-12-1986
JP 51129424	A	11-11-1976	JP 1184225 C	27-12-1983
			JP 55023790 B	25-06-1980

Patent Abstracts of Japan

PUBLICATION NUMBER : 04209717
PUBLICATION DATE : 31-07-92

APPLICATION DATE : 30-11-90
APPLICATION NUMBER : 02337724

APPLICANT : NIPPON INSULATION KK;

INVENTOR : MIYAZAKI TOMOFUMI;

INT.CL. : C01B 33/154

TITLE : PRODUCTION OF MOLDED ARTICLE OF SILICA GEL

ABSTRACT : PURPOSE: To improve insulating properties by blending aqueous slurry of secondary particles of calcium silicate crystal with an alkali silicate, then introducing CO₂ into the slurry, treating with an acid, adding a nonionic surfactant followed by molding and drying.

CONSTITUTION: A raw material of silicic acid is mixed with a raw material of lime in a molar ratio of CaO/SiO₂=0.5 to 1.5/l, optionally with an inorganic inactive substance and then blended with 10-50 times as much water as total amount of solid content to give slurry, which is subjected to hydrothermal synthesis to prepare aqueous slurry of secondary particles of calcium silicate crystal. Then the slurry is blended with an alkali silicate in an amount of give SiO₂ content in the alkali silicate to SiO₂ content in the slurry of 20/80 to 80/20. Carbon dioxide gas is introduced into the blend under pressure, the secondary particles of calcium silicate crystal is carbonated, then immersed in hydrochloric acid, treated with the acid and washed with water to give compounded secondary particle slurry of amorphous SiO₂. Then, 100 pts.wt. total amount of solid content comprising the raw material of silicic acid, the raw material of lime and the alkali silicate is blended with 2-60 pts.wt. nonionic surfactant, press-molded and dried at ≥ the decomposition temperature of nonionic surfactant to give a molded article of silica gel.

COPYRIGHT: (C)1992,JPO&Japio

XP-002137760

AN - 1977-85887Y [48]
CPY - OSAP-N
DC - L02
FS - CPI
IC - C01B33/12 ; C04B15/02 ; C04B38/06
MC - L02-G
PA - (OSAP-N) OSAKA PACKING SEIZOSHO KK
PN - JP52126695 A 19771024 DW197748 000pp
- JP61058436B B 19861211 DW198702 000pp
PR - JP19760044085 19760416; JP19840009712 19770901
XIC - C01B-033/12 ; C04B-015/02 ; C04B-038/06
AB - J52126695 The amorphous primary particle (I) of silica, has a crystalline appearance, one or more pairs of symmetrical faces, a length 1-500 μ and a depth 50 angstroms - 1 μ (the length/depth is >10). A sec. particle (II) has a dia. of 10-150 μ and is prepd. by moulding (I). (II) is a spherical particle or particle which is prepd. by compression of ca. spherical particle in one direction.
- (I), is prepd. by conversion of calcium silicate to (I) and fine particles of calcium carbonate by contacting calcium silicate with carbon dioxide in the presence of water, and sepn. by decompn. of calcium carbonate with acid.
- (I) and (II) is useful as substitute of silica gel. (I) and (II) has better properties than silica gel, such as smaller dia. of pores, larger specific surface and higher absorbing capacity for water or oil. (II) can be moulded easily from its aq. slurry contg. water/(I) 4/1-50/1. For prepn. of (I), calcium silicate and calcium carbonate are used in a ratio that CaO/SiO₂ 0.5/1-3.5/1.
IW - AMORPHOUS SILICA PARTICLE SILICA GEL SUBSTITUTE CRYSTAL APPEAR SYMMETRICAL FACE
IKW - AMORPHOUS SILICA PARTICLE SILICA GEL SUBSTITUTE CRYSTAL APPEAR SYMMETRICAL FACE
NC - 001
OPD - 1976-04-16
ORD - 1977-10-24
PAW - (OSAP-N) OSAKA PACKING SEIZOSHO KK
TI - Amorphous silica particles used as silica gel substitute - having a crystalline appearance and symmetrical faces

XP-002137761

AN - 1976-96970X [52]
CPY - OSAP-N
DC - E33 E36 L02
FS - CPI
IC - B01D53/02 ; B01J20/10 ; C01B33/12 ; C01F11/18 ; C04B15/02 ; C04B21/00
MC - E31-P03 E34-D03 L02-A02 L02-D07 L02-G12
M3 - [01] A940 C730 C108 C106 C803 C802 C807 C805 C801 C530 A220 N000 Q453
M720 M782 R034 R038 M411 M902
- [02] C800 C108 C803 C802 C807 C805 C804 B720 B831 B114 B702 N000 Q453
M720 M782 R034 R038 M411 M902
PA - (OSAP-N) OSAKA PACK MFG KK
PN - JP51129424 A 19761111 DW197652 000pp
- JP55023790B B 19800625 DW198029 000pp
PR - JP19750037477 19750327
XIC - B01D-053/02 ; B01J-020/10 ; C01B-033/12 ; C01F-011/18 ; C04B-015/02 ;
C04B-021/00
AB - J51129424 Almost spherical secondary irregular particles of Ca silicate which are formed by the three-dimensional intertwining of primary particles of calcium silicate and having 10-150 μ diameter and hollow or imcompact texture, are converted to pseudocrystalline silica gel and superfine CuCO_3 without changing the habit (sic) of calcium silicate primary particles and maintaining the form of sec. particles by forcibly carbonising in the presence of water. A product having superior mechanical strength can be obtd. by moulding and drying said cpd. material without using any binder.
IW - INDUSTRIAL PREPARATION SILICA CALCIUM CARBONATE COMPOUND PARTICLE
CONVERT CALCIUM SILICATE PSEUDO CRYSTAL SILICA GEL SUPER FINE CALCIUM
CARBONATE CARBONISE PRESENCE WATER
IKW - INDUSTRIAL PREPARATION SILICA CALCIUM CARBONATE COMPOUND PARTICLE
CONVERT CALCIUM SILICATE PSEUDO CRYSTAL SILICA GEL SUPER FINE CALCIUM
CARBONATE CARBONISE PRESENCE WATER
NC - 001
OPD - 1975-03-27
ORD - 1976-11-11
PAW - (OSAP-N) OSAKA PACK MFG KK
TI - Industrial prepn. of silica, calcium carbonate cpd. particles - by
converting calcium silicate to pseudo crystalline silica gel and super
fine calcium carbonate by carbonising in the presence of water

11-11-11

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To:

ING. BARZANO' & ZANARDO
MILANO S.P.A.
Attn. DE GREGORI, A.
Via Borgonuovo, 10
20121 Milano
ITALY

PCT Rec'd 31 JUL 2000

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT
OR THE DECLARATION

(PCT Rule 44.1)

<p>Date of mailing (day/month/year) 05/06/2000</p>	
<p>Applicant's or agent's file reference 81668</p>	<p>FOR FURTHER ACTION See paragraphs 1 and 4 below</p>
<p>International application No. PCT/EP 00/00757</p>	<p>International filing date (day/month/year) 01/02/2000</p>
<p>Applicant ITALCEMENTI S.P.A.</p>	

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within 19 months from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within 20 months from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Rec'd
PCT
31 JUL 2000

<p>Name and mailing address of the International Searching Authority</p> <p> European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016</p>	<p>Authorized officer</p> <p style="text-align: center; font-size: 1.2em;">Chantal Meyer</p>
---	--



NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

10

11

12

13

14

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

DE GREGORI, Antonella et al.
ING. BARZANO & ZANARDI
MILANO S.P.A.
Via Borgonuovo, 10
20121 Milano
ITALIE

NOT Rec'd 21 JUL 2001

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT (PCT Rule 71.1)

Date of mailing
(day/month/year) 25.04.2001

Applicant's or agent's file reference
81668

IMPORTANT NOTIFICATION

International application No.
PCT/EP00/00757

International filing date (day/month/year)
01/02/2000

Priority date (day/month/year)
03/02/1999

Applicant
ITALCEMENTI S.P.A. et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

 European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized officer

Christensen, J

Tel. +49 89 2399-8052



Ing. B. & L. MILANI
30. APR. 2001

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 81668	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP00/00757	International filing date (<i>day/month/year</i>) 01/02/2000	Priority date (<i>day/month/year</i>) 03/02/1999
International Patent Classification (IPC) or national classification and IPC C01B33/193		
Applicant ITALCEMENTI S.P.A. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 8 sheets, including this cover sheet.

- ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of ~~_____~~ sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 29/08/2000	Date of completion of this report 25.04.2001
Name and mailing address of the international preliminary examining authority: <div style="display: flex; align-items: center;"> <div> European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465 </div> </div>	Authorized officer Krafka, B Telephone No. +49 89 2399 8140



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/00757

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-22 as originally filed

Claims, No.:

1-25 as originally filed

Drawings, sheets:

1/1 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/00757

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-16,18-20,22-24
	No:	Claims	17,21,25
Inventive step (IS)	Yes:	Claims	1-16,18,22
	No:	Claims	19-20, 23-24
Industrial applicability (IA)	Yes:	Claims	1-25
	No:	Claims	

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1) Reference is made to the following documents:

D1: US-A-4 330 519 (TAKAHASHI AKIRA ET AL) 18 May 1982 (1982-05-18) & CA 1 122 779 A cited in the application

2) Novelty - Art. 33 (1) and (2) PCT

2.1. Claim 17 claims precipitated silica as a product, having purity $\geq 96\%$.

Numerous variants of manufacturing processes for precipitated silica of high purity are commonly known in the art. For example, it is remarked, that in the description, page 1 line 21 - page 2 line 18 the process of CA 1 122 779 is cited, stating on page 2 lines 17-18, that the process described allows particularly pure silica to be obtained. Additionally, D1 discloses a process to produce amorphous silica of high purity (column 2 lines 56-57), demonstrated in numerous examples, e.g. in example 2 purity is 99.3%. D1 also discloses composite materials, in which the silica is incorporated (column 2 lines 28-37). Furthermore, D1 discloses the use of said silica for various purposes, e.g. as catalyst carrier (column 5 lines 25-47). Therefore, it cannot be seen in which way Claims 17, 21 and 25 could establish novel subject-matter.

2.2. The manufacturing process as claimed in Claim 1 is considered to be novel and inventive over the processes of prior art (see, however, Item VIII). In the description, the applicant defines a process in which, among other process steps, an aqueous suspension of agglomerated particles of SiO_2 and CaCO_3 is treated with salts chosen among aluminates, borates or zincates, which results in a modification of the silica surface and an increase of its solubility in the solution. The solid phase rich in calcium carbonate can then be easily separated from the solution containing silica. Such a process step is not known from the prior art. However, reaction parameters which seem to be crucial for the success of said process are not defined in Claim 1 but are only given as optional features in subsequent dependant claims. The applicant's attention is therefore drawn to the argumentation concerning clarity of Claim 1 under Item VIII.

- 2.3. Claims 2-16 are dependent on claim 1 and as such also meet the requirements of the PCT with respect to novelty.
- 2.4. Even if the claimed process is novel and inventive, this is still not sufficient to establish novelty for the product per se and its intended use, as long as the product does not exhibit features which clearly distinguish it from the prior art and as long as the intended use is known for SiO_2 .
- 2.5. The use of precipitated silica having purity $\geq 96\%$ or of a solid phase comprising silica and calcium carbonate as additives in mixtures for tyres, in High Performance Concretes or high strength concretes has not been disclosed in the prior art. Therefore, claims 18-20 and 22-24 are considered to define novel subject-matter.

3) Inventive Step - Art. 33 (1) and (3) PCT

- 3.1. The technical problem underlying the present invention can be seen in providing an alternative procedure for preparing amorphous silica from calcium silicate. The recovery of the silica by treatment with mineral acids should be avoided, as this leads to extremely low quantities of silica obtained in comparison with the volumes of liquid involved, and the recovery of CaCO_3 , the side product, is not possible. This problem is overcome by the present invention by treating the aqueous suspension of agglomerated particles of SiO_2 and CaCO_3 , which results from the reaction of calcium silicate with CO_2 in an aqueous environment, with a salt chosen among aluminates, borates, zincates, or mixtures of the same. This reaction allows the modification of the silica surface and the increase of its concentration in the solution. The solid phase rich in calcium carbonate is separated from the solution containing silica.
- Documents D1 is considered to represent the closest prior art.
- 3.2. From none of the prior art document it appears to be obvious to treat the aqueous suspension of agglomerated particles of SiO_2 and CaCO_3 with a salt chosen among aluminates, borates, zincates, or mixtures of the same, in order to modify the silica surface and to thereby increase its concentration in the solution. Therefore, the process as claimed in independent claim 1 and in claims 2-16,

dependent on claim 1, is regarded as establishing inventive subject-matter.

- 3.3. The use of precipitated silica having purity $\geq 96\%$ or of a solid phase comprising silica and calcium carbonate as additives in mixtures for tyres has not been suggested in the prior art. Furthermore, none of the prior art documents cited above contains a hint that such kind of materials could be used in the fabrication of tyres at all. This application does not appear to lie within the scope of possible uses a person skilled in the art would take into consideration. Therefore, an inventive step is acknowledged for the subject-matter of claims 18 and 22.
- 3.4. The product of D1, which has been demonstrated to be the same as the product of the present application (see 2.1.), can be used as an additive for cements (column 5 line 29). It cannot be seen in which way the use of said silica in High Performance concretes or in high or very high strength concretes (DSP), as claimed in Claims 19 and 20, could lead to a surprising technical effect of the silica, which would be distinctively different from the technical effect achieved by the silica in D1. Therefore, an inventive step cannot be recognised for the subject-matter of Claims 19 and 20.
- 3.5. Concretes generally contain CaCO_3 and silicates. It is not clear, what technical effect could be achieved by adding a product containing just the same two constituents to concrete. Said feature is thus merely one of several straightforward possibilities from which the skilled person would select, in accordance with circumstances, without the exercise of inventive skill. Therefore, an inventive step is also not apparent for the subject-matter of Claims 23 and 24.

Re Item VII

Certain defects in the international application

- a. The terms "CEM I 52.5 (Ultracem R)" (page 20 line 21) and "Superflux 2000 AC" (page 21 line 3) employed in the description and appearing to be registered trade marks have no precise meaning as they are not internationally accepted as standard descriptive terms, thereby rendering the definition of the subject-matter of the description unclear (Article 6 PCT).

Re Item VIII

Certain observations on the international application

a. Claim 1 is unclear as to the subject-matter it refers to.

- "a compound of aluminium, boron or zinc": the description (page 6 lines 9-19) conveys the impression, that as said compound a salt should be chosen among aluminates, borates or zincates, in order to modify the silica surface and increase its concentration in the solution. Particles of insoluble Al_2O_3 for example, also falling within the scope of Claim 1 as presently drafted, do not seem to provide the technical effect mandatory for the invention claimed.

- "a calcium silicate": this vague and imprecise term casts doubt as to whether this feature is sufficiently limited in scope to enable a person skilled in the art to carry out the invention. D1, column 2 line 65 - column 3 line 57 teaches the influence of the crystalline appearance of the silicate crystals on size and shape of the silica particles produced.

- "an aqueous environment": this wording is too broad, as it does not unambiguously define that it is the suspension itself which is aqueous. Same applies to the term "neutral or basic environment".

- "treatment": any sort of measure like freezing or stirring, which do not appear to be suitable to obtain the intended product, fall within the scope of this term.

- "nanometric dimensions": concrete reaction conditions (temperature, reagent concentration, pressure and pH) appear to be missing also in step b) of Claim 1 to ensure formation of nanometer sized SiO_2 to ensure the required solubility.

- "precipitation", "drying", "gelation": in order to ensure the amorphous nature of the product it appears to be indispensable to delimit the reaction parameters under which said process features are carried out.

- Finally, the wording "procedure (...) comprising the following phases" does not make clear whether the process steps a) - f) have to be carried out in a certain order.

Summarising, it is outlined that a concrete significance in terms of a clearly defined matter for which protection is sought is not provided because the technical features necessary to perform the claimed invention (some of which are, at present, given in dependent claims) are not as a whole included in independent process claim 1.



)

9.

1

9

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP00/00757

- b. The wording of Claim 16 is unclear as it is not clear if only "adding of CO₂" is an optional feature, or if "for example" also refers to the following features of temperature and pH.
- c. In the term "max. diam. = 1200 g; 3.2 mm" it is unclear what the expression of weight is standing for.

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C.20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 11 October 2000 (11.10.00)	
International application No. PCT/EP00/00757	Applicant's or agent's file reference 81668
International filing date (day/month/year) 01 February 2000 (01.02.00)	Priority date (day/month/year) 03 February 1999 (03.02.99)
Applicant DE MARCO, Tiziana et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

29 August 2000 (29.08.00)

☐ in a notice effecting later election filed with the International Bureau on:
2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Pascal Piriou Telephone No.: (41-22) 338.83.38
---	---

PATENT COOPERATION TREATY

From the RECEIVING OFFICE

PCT

To:

De Gregorio Antonella
ING. BARZANO & ZANARDI
MILANO S.P.A.
Via Borgonuovo, 10
20121 Milano
ITALIE

PCT/RO/106
Rec'd 31 JUL 2001

INVITATION TO CORRECT DEFECTS IN THE INTERNATIONAL APPLICATION

(PCT Articles 3(4)(i) and 14(1) and Rule 26)

Date of mailing
(day/month/year)

- 9 MAR 2000

Applicant's or agent's file reference

81668

REPLY DUE

within two months
from the above date of mailing

International application No.

PCT/EP 00/ 00757

International filing date

(day/month/year) 01/02/2000

Applicant

ITALCEMENTI S.P.A.

1. ☒ The applicant is hereby invited, within the time limit indicated above, to correct, in the international application as filed, the defects specified on the attached



Annex A



Annex B1 (text matter of the international application as filed)



Annex C1 (drawings of the international application as filed)

Additional observations (if necessary):

HOW TO CORRECT THE DEFECTS ?

Correction must be submitted by filing a replacement sheet embodying the correction and a letter accompanying the replacement sheet, which shall draw attention to the difference between the replaced sheet and the replacement sheet. A correction may be stated in a letter only if it is of such a nature that it can be transferred from the letter to the record copy without adversely affecting the clarity and direct reproducibility of the sheet onto which the correction is to be transferred (Rule 26.4).

ATTENTION

Failure to correct the defects will result in the international application being considered withdrawn by this receiving Office (see Rule 26.5 for further details).

A copy of this invitation and any attachments has been sent to the International Bureau



and the International Searching Authority.

Name and mailing address of the receiving Office



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016


Authorized officer

Maria Peis

The receiving Office has found the following defects in the international application as filed:

1. As to signature* of the international application (Rules 4.15 and 90.4), the request :

- a. ☐ is not signed.
- b. ☐ is not signed by all the applicants.
- c. ☐ is not accompanied by the statement referred to in the check list in Box No. VIII of the request explaining the lack of the signature of an applicant for the designation of the United States of America.
- d. ☒ is signed by what appears to be an agent/common representative but
 - ☒ the international application is not accompanied by a power of attorney appointing him.
 - ☐ the power of attorney accompanying the international application was not signed by all the applicants.
- e. ☐ other (specify) :

 ☒ All applicants must sign, including inventors if they are also applicants (e.g. where the United States of America is designated).

2. As to indications concerning the applicant, the request (Rules 4.4 and 4.5) :

- a. ☐ does not properly indicate the applicant's name (specify) :
- b. ☐ does not indicate the applicant's address.
- c. ☐ does not properly indicate the applicant's address (specify) :
- d. ☐ does not indicate the applicant's nationality.
- e. ☐ does not indicate the applicant's residence.
- f. ☐ other (specify) :

3. As to the language of certain elements of the international application, other than the description and claims (Rules 12.1(c) and 26.3ter(a) and (c)):

- a. ☐ the request is not in a language which is both a language accepted by this receiving Office and a language of publication, which are: ENGLISH, FRENCH or GERMAN.
- b. ☐ the text matter of the drawings is not in the language in which the international application is to be published, which is: ENGLISH.
- c. ☐ the abstract is not in the language in which the international application is to be published, which is: ENGLISH.

4. The title of the invention :

- a. ☐ is not indicated in Box No.I of the request (Rule 4.1(a)).
- b. ☐ is not indicated at the top of the first sheet of the description (Rule 5.1(a)).
- c. ☐ as appearing in Box No.I of the request is not identical with the title heading the description (Rule 5.1(a)).

5. As to the abstract (Rule 8) :

- ☐ the international application does not contain an abstract.

TENT COOPERATION TREATY

From the RECEIVING OFFICE

PCT

To:

De Gregori, Antonella
ING. BARZANO' & ZANARDO
MILANO S.P.A.
Via Borgonuovo, 10
20121 Milano
ITALIE

NOTIFICATION OF THE INTERNATIONAL
APPLICATION NUMBER AND OF THE
INTERNATIONAL FILING DATE

(PCT Rule 20.5(c))

Date of mailing
(day/month/year)

- 9 MAR 2000

Applicant's or agent's file reference
81668

IMPORTANT NOTIFICATION

International application No.
PCT/ EP 00/ 00757

International filing date (day/month/year)
01/02/2000

Priority date (day/month/year)
03/02/1999

Applicant
ITALCEMENTI S.P.A.

Title of the invention

1. The applicant is hereby notified that the international application has been accorded the international application number and the international filing date indicated above.
2. The applicant is further notified that the record copy of the international application was transmitted to the International Bureau on the above date of mailing.
3. ☐ Other:

* The International Bureau monitors the transmittal of the record copy by the receiving Office and will notify the applicant (with Form PCT/IB/301) of its receipt. Should the record copy not have been received by the expiration of 14 months from the priority date, the International Bureau will notify the applicant (Rule 22.1(c)).

Name and mailing address of the receiving Office



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Maria Pais

PCT
PCT/RO/101 Rec'd 31 JUL 2001

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only	
PCT/EP 00 / 00757	
International Application No.	
01 FEB 2000	(01 02 2000)
International Filing Date	
EUROPEAN PATENT OFFICE	
Name of receiving Office and PCT International Application	
Applicant's or agent's file reference (if desired) (12 characters maximum)	
81668	

Box No. I TITLE OF INVENTION	
PROCEDURE FOR PREPARING SILICA FROM CALCIUM SILICATE	
Box No. II APPLICANT	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	
ITALCEMENTI S.p.A. Via G. Camozzi 124 I- 24100 BERGAMO, Italy	
<input type="checkbox"/> This person is also inventor.	
Telephone No.	
Facsimile No.	
Teleprinter No.	
State (that is, country) of nationality: IT	
State (that is, country) of residence: IT	
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input checked="" type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box.	
Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	
DE MARCO Tiziana Via Lungo Brembo 34 I- 24035 CURNO, BERGAMO Italy	
This person is: <input type="checkbox"/> applicant only <input checked="" type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only (If this check-box is marked, do not fill in below.)	
State (that is, country) of nationality: IT	
State (that is, country) of residence: IT	
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input checked="" type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box.	
<input type="checkbox"/> Further applicants and/or (further) inventors are indicated on a continuation sheet.	
Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE	
The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: <input checked="" type="checkbox"/> agent <input type="checkbox"/> common representative	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)	
DE GREGORI Antonella APPOLONI Romano PARISI Luigi ZANARDO Giovanni FUSINA Gerolamo	
ING. BARZANO' & ZANARDO MILANO S.p.A. Via Borgonuovo 10 I- 20121 MILAN, Italy	
Telephone No. 02 6554287	
Facsimile No. 02 6598859	
Teleprinter No.	
<input type="checkbox"/> Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.	



Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet should not be included in the request.

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

GRONCHI Paolo
Via Solari 2/a
I- 20144 MILAN, Italy

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

IT

State (that is, country) of residence:

IT

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

CASSAR Luigi
Via Europa 42
I- 20097 SAN DONATO MILANESE, MILAN
Italy

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

IT

State (that is, country) of residence:

IT

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.



12



Box No. V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes: at least one must be marked):

Regional Patent

- ☒ AP ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SL Sierra Leone, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☒ EA Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ EP European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ OA OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line):

- | | |
|--|--|
| <input checked="" type="checkbox"/> AE United Arab Emirates | <input checked="" type="checkbox"/> LR Liberia |
| <input checked="" type="checkbox"/> AL Albania | <input checked="" type="checkbox"/> LS Lesotho |
| <input checked="" type="checkbox"/> AM Armenia | <input checked="" type="checkbox"/> LT Lithuania |
| <input checked="" type="checkbox"/> AT Austria | <input checked="" type="checkbox"/> LU Luxembourg |
| <input checked="" type="checkbox"/> AU Australia | <input checked="" type="checkbox"/> LV Latvia |
| <input checked="" type="checkbox"/> AZ Azerbaijan | <input checked="" type="checkbox"/> MD Republic of Moldova |
| <input checked="" type="checkbox"/> BA Bosnia and Herzegovina | <input checked="" type="checkbox"/> MG Madagascar |
| <input checked="" type="checkbox"/> BB Barbados | <input checked="" type="checkbox"/> MK The former Yugoslav Republic of Macedonia |
| <input checked="" type="checkbox"/> BG Bulgaria | |
| <input checked="" type="checkbox"/> BR Brazil | <input checked="" type="checkbox"/> MN Mongolia |
| <input checked="" type="checkbox"/> BY Belarus | <input checked="" type="checkbox"/> MW Malawi |
| <input checked="" type="checkbox"/> CA Canada | <input checked="" type="checkbox"/> MX Mexico |
| <input checked="" type="checkbox"/> CH and LI Switzerland and Liechtenstein | <input checked="" type="checkbox"/> NO Norway |
| <input checked="" type="checkbox"/> CN China | <input checked="" type="checkbox"/> NZ New Zealand |
| <input checked="" type="checkbox"/> CU Cuba | <input checked="" type="checkbox"/> PL Poland |
| <input checked="" type="checkbox"/> CZ Czech Republic | <input checked="" type="checkbox"/> PT Portugal |
| <input checked="" type="checkbox"/> DE Germany | <input checked="" type="checkbox"/> RO Romania |
| <input checked="" type="checkbox"/> DK Denmark | <input checked="" type="checkbox"/> RU Russian Federation |
| <input checked="" type="checkbox"/> EE Estonia | <input checked="" type="checkbox"/> SD Sudan |
| <input checked="" type="checkbox"/> ES Spain | <input checked="" type="checkbox"/> SE Sweden |
| <input checked="" type="checkbox"/> FI Finland | <input checked="" type="checkbox"/> SG Singapore |
| <input checked="" type="checkbox"/> GB United Kingdom | <input checked="" type="checkbox"/> SI Slovenia |
| <input checked="" type="checkbox"/> GD Grenada | <input checked="" type="checkbox"/> SK Slovakia |
| <input checked="" type="checkbox"/> GE Georgia | <input checked="" type="checkbox"/> SL Sierra Leone |
| <input checked="" type="checkbox"/> GH Ghana | <input checked="" type="checkbox"/> TJ Tajikistan |
| <input checked="" type="checkbox"/> GM Gambia | <input checked="" type="checkbox"/> TM Turkmenistan |
| <input checked="" type="checkbox"/> HR Croatia | <input checked="" type="checkbox"/> TR Turkey |
| <input checked="" type="checkbox"/> HU Hungary | <input checked="" type="checkbox"/> TT Trinidad and Tobago |
| <input checked="" type="checkbox"/> ID Indonesia | <input checked="" type="checkbox"/> UA Ukraine |
| <input checked="" type="checkbox"/> IL Israel | <input checked="" type="checkbox"/> UG Uganda |
| <input checked="" type="checkbox"/> IN India | <input checked="" type="checkbox"/> US United States of America |
| <input checked="" type="checkbox"/> IS Iceland | |
| <input checked="" type="checkbox"/> JP Japan | <input checked="" type="checkbox"/> UZ Uzbekistan |
| <input checked="" type="checkbox"/> KE Kenya | <input checked="" type="checkbox"/> VN Viet Nam |
| <input checked="" type="checkbox"/> KG Kyrgyzstan | <input checked="" type="checkbox"/> YU Yugoslavia |
| <input checked="" type="checkbox"/> KP Democratic People's Republic of Korea | <input checked="" type="checkbox"/> ZA South Africa |
| | <input checked="" type="checkbox"/> ZW Zimbabwe |
| <input checked="" type="checkbox"/> KR Republic of Korea | |
| <input checked="" type="checkbox"/> KZ Kazakhstan | |
| <input checked="" type="checkbox"/> LC Saint Lucia | |
| <input checked="" type="checkbox"/> LK Sri Lanka | |

Check-boxes reserved for designating States which have become party to the PCT after issuance of this sheet:

☒ COSTA RICA TANZANIA MOROCCO

☒ DOMINICAN REPUBLIC

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation of a designation consists of the filing of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)

Box No. VI PRIORITY CLAIM		<input type="checkbox"/> Further priority claims are indicated in the Supplemental Box		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application: regional Office	international application: receiving Office
item (1) ^{03 FEB 99} (03/02/1999)	MI99A000197	ITALY		
item (2)				
item (3)				

☐ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s):

* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA / EPO

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year)

Number

Country (or regional Office)

Box No. VIII CHECK LIST: LANGUAGE OF FILING

This international application contains the following number of sheets:

request : 4
description (excluding sequence listing part) : 22
claims : 4
abstract : 1
drawings : 1
sequence listing part of description : 1

Total number of sheets : 32

This international application is accompanied by the item(s) marked below:

- ☒ fee calculation sheet
- ☒ separate signed power of attorney follows
- ☐ copy of general power of attorney; reference number, if any:
- ☐ statement explaining lack of signature
- ☒ priority document(s) identified in Box No. VI as item(s): follows
- ☐ translation of international application into (language):
- ☐ separate indications concerning deposited microorganism or other biological material
- ☐ nucleotide and/or amino acid sequence listing in computer readable form
- ☒ other (specify): letter

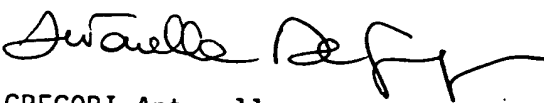
Figure of the drawings which should accompany the abstract: 1

Language of filing of the international application:

ENGLISH

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).


DE GREGORI Antonella

31 JAN 2000

For receiving Office use only		2. Drawings: <input checked="" type="checkbox"/> received: <input type="checkbox"/> not received:
1. Date of actual receipt of the purported international application:	01 FEB 2000 (01.02.2000)	
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:		
4. Date of timely receipt of the required corrections under PCT Article 11(2):		
5. International Searching Authority (if two or more are competent): ISA /	6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid.	

Date of receipt of the record copy by the International Bureau:

For International Bureau use only

